15

X-RAY INVESTIGATION OF THE PARA-DIHALOGEN DERIVATIVES OF DIPHENYL

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ABSTRACT. The isomorphous crystals of 4-4′-difluoro-diphenyl, 4-4′-dichloro-diphenyl and 4-4′-dibromo-diphenyl have been studied by X-ray methods. The dimensions of the unit cell have been found in each case. They point to the presence of 8 molecules per unit cell. The crystal of 4-4′-dichloro-diphenyl has been further studied by the moving film camera. The absence of reflections (oko) in odd orders suggests that this crystal belongs to the space group C_{2h}^{5} ($P\,2_1/m$) of the monoclinic holohedral class.

INTRODUCTION

In diphenyl (Dhar, 1932) as well as in terphenyl (Picket, 1933) and quaterphenyl (Picket, 1926) the two benzene rings lie in a plane and are linearly extended. In dibenzyl (Dhar, 1934; Robertson, 1934 and 1935) due to the introduction of the two aliphatic carbon atoms the rings deviate appreciably from the mean plane on opposite sides. In striking contrast with the structure of dibenzyl, the benzene rings have been found by Robertson to be almost coplanar in stilbene (Robertson and Woodward, 1937).

It would be of interest to find if the simple substitution of some of the hydrogen atoms in diphenyl would affect its planar and linearly extended structure. For this purpose 4-4′ disubstituted compounds of diphenyl would naturally be the simplest and among them the difluoro, dichloro- and dibromo-derivatives form a good series of isomorphous monoclinic crystals. They have, therefore, been chosen for the X-ray study. It is proposed to give in this paper an account of the preliminary investigation made with the crystals of these substances.

UNIT CELL AND DIMENSIONS

As reported in Groth's Chemische Krystallographie (1905) all the crystals belong to the monoclinic prismatic class. Crystals of 4-4′ dichloro-diphenyl and 4-4′ dibromo-diphenyl have been grown out of the solution of alcohol and benzene by slow evaporation. They have been obtained as prisms elongated along the *c*-axis with a (100) face bounded by q (011) and seldom r (101) faces. Sufficiently good single crystals of 4-4′ difluoro-diphenyl could not be obtained after several trials. Consequently for this crystal only Debye-Sherrer powder diagram was taken. The other two crystals were studied by the rotating crystal method. The copper K-radiation was used. It was filtered through a nickel foil whenever necessary.

The dimensions of the unit cells of three crystals are given in the following table :—

TABLE I

Crystal	Sp. gr.	'a'	'b'	'c'	β	Number of Molecules per unit-cell
4-4′ Difluoro-diphenyl	1.361	14.83 Å	13.30 Å	9.45 Å	96°8′	8
4-4′ Dichloro-diphenyl	1.439	15.94 Å	13.61 Å	9.79 Å	96°48′	8
4-4′ Dibromo-diphenyl	1.897	15.80 Å	14.09 Å	9.82 Å	94°30′	8

The data for the dichloro- and the dibromo- derivatives were obtained from the rotation pictures, assuming the values of β as given in Groth's Kristallographie. The values of β were later on confirmed from the measured spacings of some axial planes identified in the rotation photographs. Specific gravity values in column 2 have been taken from the Groth's book.

For the difluoro-derivative for which only the powder photopraph was taken the dimensions of the unit cell cannot, of course, be uniquely determined. Since it is isomorphous with the other two crystals, the different spacings observed could be identified by comparing them with the latter crystals, The observed spacings for the difluoro derivative and those calculated on the basis of the cell dimensions given in Table I are given below :

TABLE II

Powder photograph of 4-4′-difluoro-diphenyl (with nickel filter)

Serial No.	Observed (Bragg angle)	Spacing observed	Spacing calculated	Planes assigned	Remarks on intensity
1	9°26′	4.695 Å	(4.695 Å)	002	v. s.
2	10°31′	4.216 Å	4.17 Å	202	s.
3	12°03′	3.686 Å	(3.686 Å)	400	v.s.
4	14°25′	3.090 Å	3.13 Å	003	m.
5	16°11′	2.777 Å	2.76 Å	340	w.
6	17°49′	2 515 Å	2.46 Å	600	w.
7	20°19′	2.217 Å	(2.217 Å)	060	m.
	23°28′	1.932 Å	...	...	v.w.

For a detailed study of the crystal structure, 4-4′-difluoro-diphenyl would have been the most suitable among the three isomorphous derivatives of diphenyl because of its least absorption of X-rays. But unfortunately sufficiently good single crystals of difluoro-derivatives were not available. So 4-4′-dichloro-diphenyl, being next in order of absorption was chosen and studied in detail.

WEISSENBERG PHOTOGRAPHS AND THE INDEXING OF THE REFLECTED SPOTS

Weissenberg photographs of the zero layerline of 4-4′-dichlorodiphenyl were taken adout the '*b*' and '*c*' axes. In these photographs reflexions from the axial and prism planes only are present. In order to study the general planes another Weissenberg photograph of the first layerline of the crystal about the '*b*' axis was taken.

To identify the reflecting planes to which the spots are due in the zero layerline of the Weissenberg photograph the most straightforward method which is indeed an adaptation of the method described by Bernal (1927) is used. The perpendicular distance ξ_ω from the central line in the diagram for each spot is read and then converted into the ξ value with the help of the relation

$$\frac{\xi_\omega}{2\pi r_F} = \frac{\theta}{180} \qquad \ldots (1)$$

$$\xi = 2\sin\theta \qquad \ldots (2)$$

The ξ value of each plane can also be calculated from the reciprocal lattice canstants of the crystal as for example for rotation about the '*c*' axis of the crystal.

$$\xi = \{k^2 b^{*2} + (ha^* + lc^* cos\beta^*)^2\}^{\frac{1}{2}}$$

The comparision between the observed and calculated ξ values makes the assignment of the indices to the planes of the respective spots possible.

For the first layerline weissenberg diagram about the '*b*' axis, the experimental values of Bragg angle θ were deduced by measurement of ξ_ω values for the various spots from (1). They were then compared with the calculated values of the Bragg angle from the relation

$$\mathrm{Sin}^2\theta_{hll} = \frac{\lambda^2}{4\sin^2\beta}\left[\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl}{ac}\cos\beta + \frac{\sin^2\beta}{b^2}\right]$$

Where the terms have the usual significance.

A chart has also been prepared on the basis of Wooster and Wooster's (1933) method, corelating the Bragg angle of reflexion θ instead of ξ_ω against the angle of rotation of the crystal and the two series of curves are drawn.

The photographic film is laid over the graphical chart so drawn and the correct assignment of the indices is confirmed as the spots all lie on the intersections of the two series of curves. For the zero layerline Weissenberg diagram about the '*b*' axis, one series of curves runs with (n o l) and another with (h o n) where n is a constant along any one curve while h or l changes by steps of unity.

The Weissenberg diagrams are in this way deciphered and the reflecting planes so obtained are entered in the following Tables III, IV and V.

TABLE III

Weissenberg photograph of the zero layerline of 4-4'-dichloro-diphenyl crystal about '*c*' axis.

Axial Planes	Prism Planes	Prism Planes	Prism Planes
400 (v. s.)	140 (v. s.)	340 (s)	530 (w.m.)
600 (w)	180 (m)	380 (w)	540 (w.m.)
800 (m)	250 (m)	410 (m)	610 (w.m.)
040 (m)	270 (s)	430 (w.m.)	760 (w)
080 (w m.)	310 (m)	440 (m)	810 (w)
0(10)0 (v.w)	330 (w)	510 (w.m.)	
0(12)0 (w m.)			

TABLE IV

Weissenberg photograph of the zero layerline of 4-4'-dichloro-diphenyl about '*b*' axis.

Axial Planes	Prism Planes	Prism Planes
400 (s)	102 (v.s.)	$40\bar{1}$ (v.w.)
600 (v.w.)	$10\bar{3}$ (s)	402 (s)
800 (m)	106 (w.m.)	$60\bar{2}$ (m)
(12)00 (w)	201 (m)	$60\bar{4}$ (w)
(16)00 (w)	204 (m)	$80\bar{2}$ (w)
002 (v w.)	$20\bar{4}$ (w)	(10)$0\bar{3}$(v.w.)
004 (w)	302 (s)	(10)05(v.w)
	306 (w)	

TABLE V

Weissenberg photograph of the 1st layer-line of 4-4′-dichloro-diphenyl about '*b*' axis.

Prism Planes	General Planes	General Planes	General Planes
$01\bar{6}$ (w)	$11\bar{2}$ (w.m.)	314 (w.m.)	$71\bar{2}$ (v.w)
$01\bar{7}$ (w)	$11\bar{3}$ (w.m.)	$31\bar{5}$ (w.m.)	713 (w)
310 (w)	$11\bar{4}$ (w)	$\bar{3}1\bar{5}$ (v.w.)	714 (v w)
510 (s)	$11\bar{5}$ (v.w.)	511 (w)	$71\bar{4}$ (w)
710 (v.w.)	$\bar{1}1\bar{8}$ (v,w.)	$51\bar{1}$ (v.w.)	811 (v.w.)
810 (w)	$\bar{2}1\bar{4}$ (w)	$51\bar{2}$ (s)	$81\bar{1}$ (w)
(14)10 (v.w.)	$\bar{2}1\bar{9}$ (w)	$51\bar{3}$ (w)	812 (w)
	$21\bar{6}$ (v.w.)	514 (w.m.)	$81\bar{2}$ (w m.)
	311 (w)	$51\bar{4}$ (w)	$81\bar{3}$ (w)
	212 (w m.)	$51\bar{6}$ (v.w.)	(10)11 (w)
	$31\bar{2}$ (v.w.)	$51\bar{8}$ (v.w.)	(10)14 (w)
	313 (s)	711 (v.w.)	(12)12 v w.)
	$31\bar{3}$ (s)	$71\bar{1}$ (v.w.)	(14)11 (v.w)

It is evident from the above tables that all planes of the type (oko) are absent when k is odd. In addition, planes of the type (hoo) as well as (ool) have also been found to be absent when h or l is odd. But because the latter planes are not symmetry planes their absence is not significant and is regarded as accidental. The crystal of 4-4′-dichlorodiphenyl is consequently assigned to the spacegroup C_{2h}^{2} ($P2_1/m$) of the monoclinic holohedral class.

The study of the 4-4′-dibromo-diphenyl crystal by the moving-film camera is in progress.

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